

HYDROGEN ATOM REACTIONS WITH  
ELEMENTAL CARBON AT 77°K

by

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## INTRODUCTION AND REVIEW OF LITERATURE

### Surface Properties of Carbon

The various forms of carbon, with the exception of diamond, are well known adsorbents, and both physical adsorption and chemisorption can occur. According to the work of Lowery and Hullett (1), after charcoal has been outgassed thoroughly at 900-1000°C and has been allowed to cool in vacuum to room temperature, such gases as hydrogen, nitrogen and carbon monoxide can be admitted and subsequently released at room temperature. The adsorption of the gases is clearly no more than physical. Yet surface films held by primary valences evidently occur since large quantities of hydrogen and oxides of carbon are released during the degassing of charcoal at 600-1200°C. Nitrogen also is released in the degassing of graphite at temperatures up to 2200°C, and this is the predominant gas evolved in the range 1700-2200°C.

The clean up of hydrogen by fresh carbon or graphite wear-dust (2) at room temperature has been interpreted as a chemical adsorption resulting from the opening of the graphite lattice during the process of frictional seizure. The amount of hydrogen adsorbed by the dust was found to be  $10^5$  times greater than that adsorbed by a typical activated charcoal at the same temperature and pressure. It is known from electron microscope studies that in graphite wear-dust a large range of sizes is present extending from 1000Å down to 100Å or less in diameter.

A number of particles semi-transparent to the electron beam are present and these are certainly of a thickness considerably less than  $100\overset{\circ}{\text{A}}$ .

The sorption of hydrogen by coconut-charcoal at temperatures of liquid air has been investigated by McBain and Firth (3). In both cases it was observed that equilibrium was attained only after a lapse of many hours. According to McBain, most of the gas is condensed instantaneously on the surface (true adsorption); this is followed by a gradual diffusion of hydrogen into the charcoal at a rate which obeys the regular laws of diffusion. This last stage corresponds to solution of the gas between carbon atoms, and McBain concluded that this solubility is proportional to the square root of the pressure, indicating that the dissolved gas is in the atomic condition.

Lowery and Morgan (3) have compared the sorptive capacity of graphite with that of coconut-charcoal. Even at the temperature of liquid air the hydrogen adsorption by graphite is only about 1/10 of that observed for activated charcoal.

#### Reactions of Atomic Species with Carbon

A survey of the literature reveals that the reactions of atomic species with solid carbon are not well characterized. There have been occasional publications in this field, but the information available so far is very slight.

Avramenko was the first to report the direct reaction between atomic hydrogen and soot at a temperature of  $100^{\circ}\text{C}$  (4).



The reaction was carried out in a glow discharge. He found that the reaction products showed an absorption band at  $4317\overset{\text{O}}{\text{\AA}}$  indicating the presence of CH radicals. Harris and Tickener (5) reacted soot with hydrogen atoms. They found the main product to be methane. A higher molecular weight fraction (volatile at  $-100^{\circ}\text{C}$ ) was about 8% by volume of the total.

Blackwood and McTaggart (6) prepared char at different temperatures, and reacted the carbon with hydrogen atoms. They found that, unlike molecular hydrogen (7), there was not a great variation in the rate of formation of methane with the different char preparations. The only product which they mentioned was methane. These experiments were carried out at pressure of 0.3-0.5 torr (mm of mercury). A radiofrequency discharge was used to dissociate hydrogen. About 0.5-1.0 g of char was used each time.

It was reported by Walker, Jr., et al. (8) that hydrogen atoms produced by the action of microwave discharge on hydrogen gas can react with carbon only when the latter is in the plasma. A similar observation has been made by Shahin (9). Shahin found that the products of the reaction were  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ . He proposed that atomic carbon vapors reacted with hydrogen atoms to give methane. Acetylene arose either from the reaction of  $\text{C}_2$  species with hydrogen or by attack of monoatomic carbon on newly formed methane. That the latter reaction was indeed significant was borne out by the fact that the relative abundance of acetylene was increased when the hydrogen pressure was reduced.

This is in conformity with the presence of carbon atoms as they are expected to undergo C-H bond insertion reactions with methane to form acetylene. Walker, Jr. and his co-workers (10) have reported  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$  to be the major products. However, they also detected ethane, propyne and isopentane.

A. B. King and Henry Wise (11) have studied the kinetics of reactions of hydrogen atoms with evaporated carbon films in the temperature range 365-500°K and at a total gas pressure of 0.02 to 0.10 torr. The removal of carbon by chemical reaction, as detected by the variation of film thickness with time, was found to occur at two distinct rates with activation energies of 9.2 and 7.1 kcal/mole.

Reactions with carbon of atomic species other than hydrogen have also been studied (10, 12). Oxygen atoms produced by radiofrequency or microwave discharges reacted with graphite at room temperature. Carbon monoxide was the main product along with some  $\text{CO}_2$ . The reaction of carbon with the products of a water discharge (12) underscores the differences in reactivity of carbon between a hydrogen discharge and an oxygen discharge. The water discharge conveniently serves as a simultaneous source of both hydrogen atoms and an active oxygen species. When the carbon sample is placed outside the discharge zone, the hydrogen atoms recombine, as in a hydrogen discharge, and the active oxygen species react with the carbon to produce primarily CO.

## The Present Work and its Object

The object of the present work was to find more details of hydrogen atom reaction with carbon. In this study hydrogen atoms were reacted with various forms of carbon. Reactions were carried out with hydrogen atoms of different energies. Also the effect of the variation of hydrogen pressure on products was studied. Methane,  $C_2H_6$ ,  $C_3H_8$ ,  $n-C_4H_{10}$  were identified to be the principal reaction products, and their relative yields were calculated.

## EXPERIMENTAL

### Materials

Lamp Black. The lamp black used was collected from the flame of a burner by using the flame to bathe the glass surface which formed the target.

Graphite. A disc of graphite (Great Lakes Graphite, nuclear grade) was cut from a large piece and fastened to the lower end of a brass tube with screws to form the target C (Plate I). The disc snugly fitted the brass surface. The lower end of the brass tube was vacuum tight.

Diamond Dust. The diamond dust used was purchased from DIA-DUSCO. The 100-mesh product was stuck to the glass surface with water glass.

Tritium Supply. To prepare molecular hydrogen containing tritium, 5  $\mu$ l of tritiated water (specific activity 18 mc/mmole)



was reduced by metallic zinc in an evacuated Pyrex (#1720) fusion tube at 650°C. The fusion tube was placed in a bigger Pyrex tube and the latter was then evacuated. The fusion tube was broken inside by carefully striking its weak (sealed) end against the wall. The flow of tritium into the reaction vessel was controlled by a stopcock and then by a high vacuum needle valve (V in Plate I). The hydrogen was atomized on a hot tungsten filament F (Plate I).

### Apparatus

The pressure measurements were carried out using a Pirani gauge (Consolidated Electronics Model GP-110). The Pirani gauge was calibrated with a McLeod gauge. The calibration stayed constant when checked after regular intervals, but a zeroing adjustment was needed frequently. The temperature of the tungsten filament was measured using an optical pyrometer (Leeds and Northrup Co., Cat. #8622-C). Corrections for emissivity were made.

The reaction vessel and other apparatus are shown in Plate I and the analysis assembly is described in Fig. 1.

### Experimental Procedure

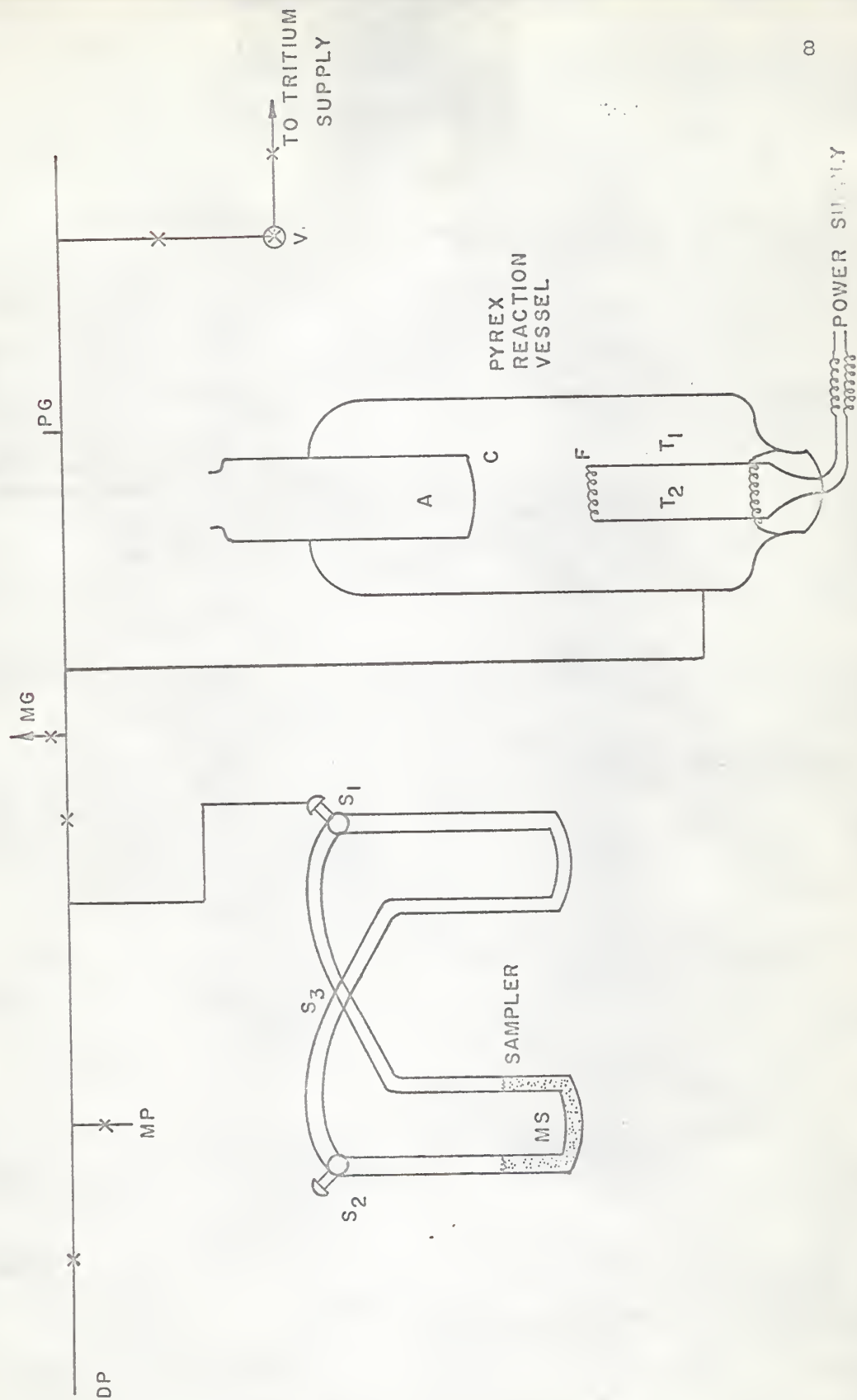
Before each reaction the carbon target was heated to 250°C and all parts of the vacuum system were evacuated to a pressure less than  $10^{-5}$  torr. About two minutes before the experiment, liquid nitrogen was added to the tube A (Plate I) to cool the target to 77°K. The required amount of hydrogen was let in by



# EXPLANATION OF PLATE I

DP	-	mercury diffusion pump
MP	-	mechanical vacuum pump
X	-	stopcocks
MG	-	McLeod gauge
PG	-	Pirani vacuum gauge
V	-	high vacuum needle valve (Will Scientific, Inc. cat. #8)
S <sub>1</sub> , S <sub>2</sub>	-	three-way stopcocks
MS	-	Molecular Sieve, Linde type 5A
C	-	carbon target
A	-	Pyrex tube
T <sub>1</sub> , T <sub>2</sub>	-	tungsten leads
F	-	0.03" tungsten filament
S <sub>3</sub>	-	four-way stopcock

# PLATE I

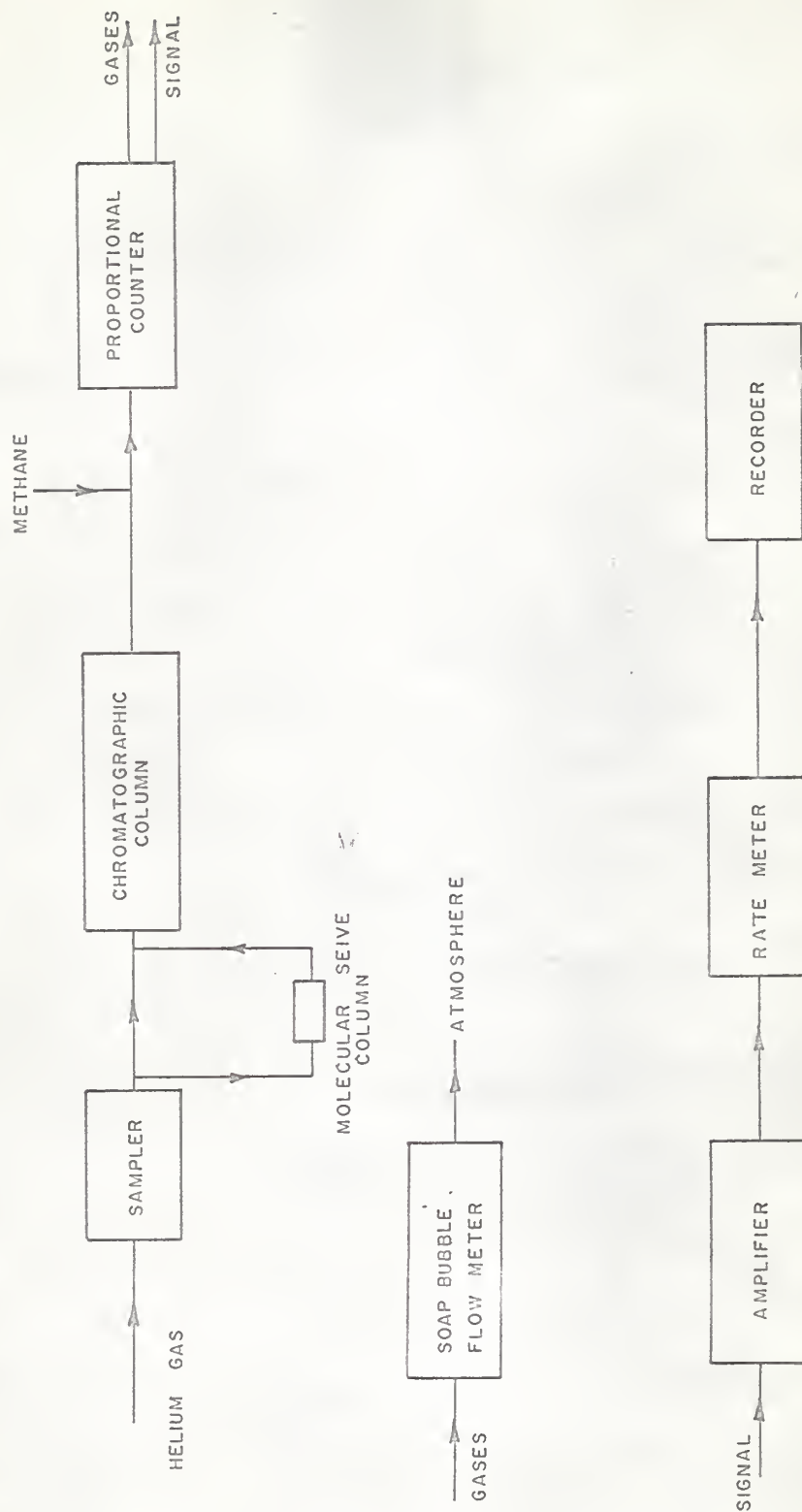


adjustment of the needle valve V. The hydrogen pressure was read on the Pirani gauge. The filament was turned on, and an electric timer was started. At the end of five minutes the filament was turned off, and the liquid nitrogen in the tube A was sucked off by a water aspirator. The target was heated to about 250°C with a specially designed electric heater to release the hydrocarbon products.

The hydrocarbons from the reaction vessel were led into the sample consisting of two U-tubes (plate I). The U-tube farther removed from the reaction vessel contained Molecular Sieve 5A. Both the U-tubes were cooled by liquid nitrogen. In this way C<sub>2</sub> and higher hydrocarbons were entrapped in the first U-tube whereas methane (and some hydrogen) was entrapped in the second U-tube. The analysis was carried out according to the scheme shown in Fig. 1. First the U-tube containing the methane and hydrogen mixture was flushed with the carrier gas (helium). Then the gases were led to the chromatographic column through the 2-foot column of Molecular Sieve Linde type 5A, which separated methane from hydrogen. The tritium activity was then counted by the proportional counter as is shown in Figure 1. The signal from the ratemeter was used to drive the recorder.

For the identification of products, gas chromatographic analyses were carried out using two different columns: a 10-foot squalane and a 15-foot dimethylsulfolane column. Then the retention time of products were compared with the retention times of known compounds on the same two columns measured under the same conditions of

FIG. 1. A FLOW SHEET OF THE ANALYSIS ASSEMBLY





column temperature and carrier gas flow rate. (See Table I)

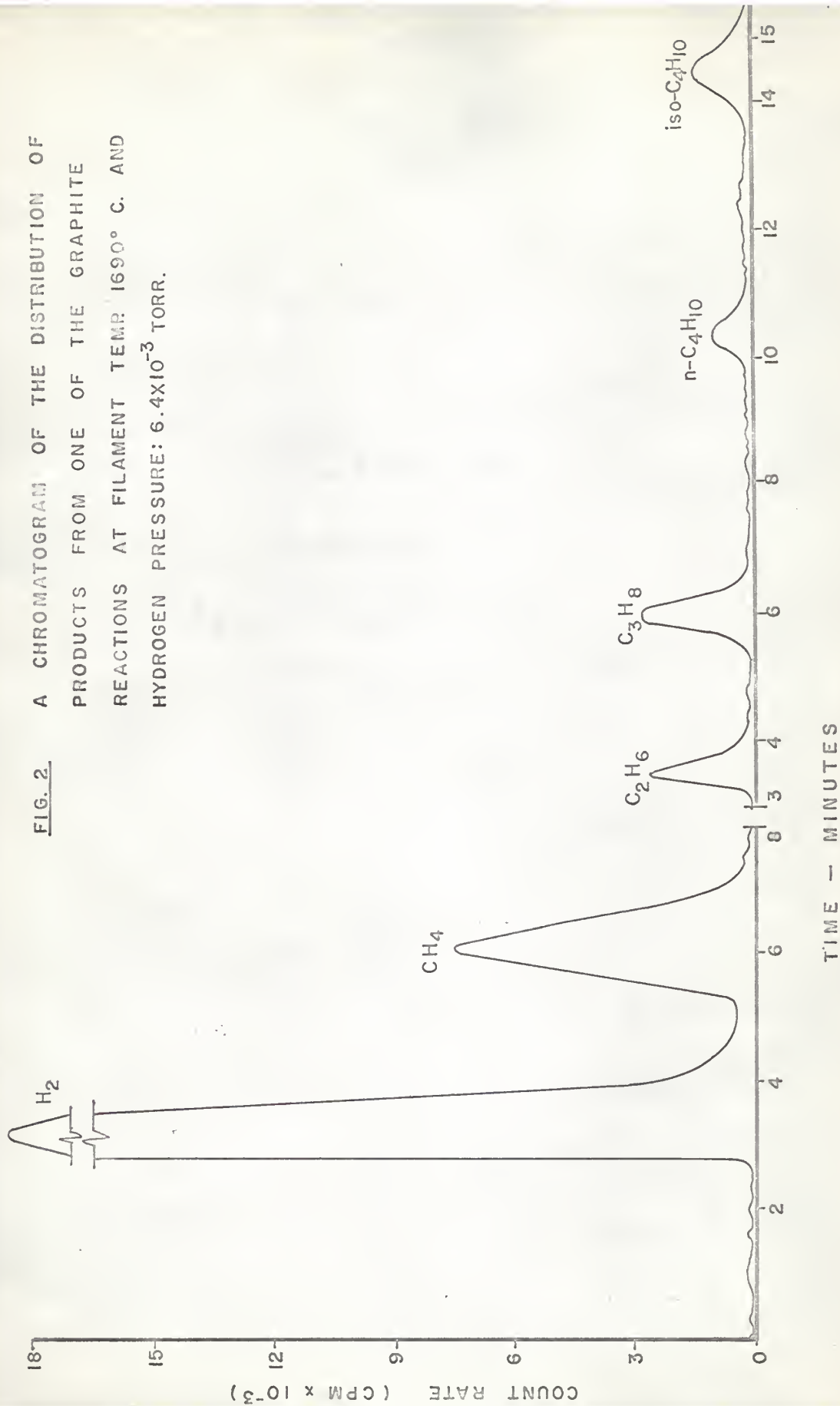
Table I. Retention volumes of hydrocarbons.

COMPOUND	RETENTION VOLUME (ml) on 10-foot squalane column	RETENTION VOLUME (ml) on 15-foot D.M.S. column
CH <sub>4</sub>	74	
C <sub>2</sub> H <sub>6</sub>	82 (82) *	105 (104)
C <sub>3</sub> H <sub>6</sub>	133	
C <sub>3</sub> H <sub>8</sub>	156 (149)	135 (137)
iso- C <sub>4</sub> H <sub>10</sub>	261 (252)	180 (181)
n - C <sub>4</sub> H <sub>10</sub>	371 (364)	234 (228)
1-butene	334	
Trans-2-butene	449	
Isobutene		314
Cis-2-butene	503 (487)	442 (443)
Neopentane	460	
Isopentane	883	
n-pentane	1432	

\* Retention volumes of radioactive products of H atom reactions with elemental carbon appear in parentheses.

The small differences between the retention volumes of known compounds and the unknowns may be due to small differences in the room temperature and/or other minor adjustments in the operating conditions (since the measurements were not made on the same day).

In Fig. 2 is given a typical chromatogram from the 10-foot



squalane column at a flow of 24 ml/min.

The quantitative entrapping of methane was shown by another experiment. Some methane (same grade as used in the proportional counter, The Matheson Company, Inc. technical grade) was let into the vacuum system. A part of this was held behind the needle valve V (Plate I). Then the entire system along with the sampler was evacuated. Methane was let into the system until a pressure of  $5 \times 10^{-3}$  torr was reached. Then the methane was entrapped in the same way as was done in the regular experiments. The pressure on the Pirani gauge dropped down to less than  $10^{-5}$  torr assuring that methane was completely entrapped.

In the experiments using helium as moderator, a different reaction vessel was used. A round Pyrex flask surrounded the tungsten filament. The flask could be cooled in a liquid nitrogen bath. The hydrogen was let into the reaction vessel first, then helium (about 0.13 torr) was let in to act as a moderator. The rest of the procedure was the same as described previously.

## RESULTS

The data are presented in Tables 2-5. The error values given are the average deviations from the average value of 2-6 determinations. The percentages of various compounds were calculated on the basis of the distribution of radioactivity. In addition to the products given in the tables ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $n\text{-C}_4\text{H}_{10}$ , iso- $\text{C}_4\text{H}_{10}$  and Cis-2-butene), it was anticipated that some high molecular weight compounds (polymeric perhaps) might

Table 2. Products of hydrogen atom reactions with graphite, carbon black and diamond dust at 77°K. Effect of the variation of filament temperature. The reaction time was 5 minutes and the initial hydrogen pressure was  $3.2 \times 10^{-3}$  torr.

Product	Filament temperature		
	1400°C	1670°C	2037°C
<u>Graphite</u>	%	%	%
CH <sub>4</sub>	81.0 ± 0.9	63.5 ± 2.2	55.1 ± 0.8
C <sub>2</sub> H <sub>6</sub>	14.8 ± 1.4	16.9 ± 1.4	20.4 ± 0.9
C <sub>3</sub> H <sub>8</sub>	4.2 ± 0.9	12.0 ± 1.4	15.6 ± 1.4
cis-2-butene	---	---	---
iso-C <sub>4</sub> H <sub>10</sub>	---	4.0 ± 0.2	2.7 ± 0.8
n-C <sub>4</sub> H <sub>10</sub>	---	3.6 ± 0.4	6.2 ± 0.7
Relative total yield	47 ± 14	130 ± 23	212 ± 21
<u>Carbon Black</u>			
CH <sub>4</sub>	83.4 ± 0.3	68.8 ± 3.6	68.4 ± 2.7
C <sub>2</sub> H <sub>6</sub>	12.7 ± 1.4	16.2 ± 1.1	15.3 ± 0.4
C <sub>3</sub> H <sub>8</sub>	3.9 ± 1.1	8.7 ± 3.5	9.2 ± 1.1
cis-2-butene	---	---	---
iso-C <sub>4</sub> H <sub>10</sub>	---	1.8 ± 0.9	1.5 ± 0.3
n-C <sub>4</sub> H <sub>10</sub>	---	4.5 ± 0.9	5.6 ± 1.6
Relative total yield	32 ± 7	38 ± 12	69 ± 9
<u>Diamond Dust</u>			
CH <sub>4</sub>	85.5	66.1 ± 4.2	64.5 ± 4.2
C <sub>2</sub> H <sub>6</sub>	11.5	20.3 ± 1.2	19.3 ± 6.9
C <sub>3</sub> H <sub>8</sub>	3.5	8.4 ± 2.2	9.8 ± 2.8
cis-2-butene	---	---	---
iso-C <sub>4</sub> H <sub>10</sub>	---	2.2 ± 0.6	3.8 ± 1.8
n-C <sub>4</sub> H <sub>10</sub>	---	3.0 ± 0.4	2.6 ± 0.2
Relative total yield	60 ± 12	64 ± 9	80 ± 8



Table 3. Products of hydrogen atom reactions with graphite at 77°K. Effect of hydrogen pressure variation. Reaction time was 5 minutes and filament temperature was 1590°C.

Product	Initial Hydrogen Pressure		
	: 3.2x10 <sup>-3</sup> torr	: 6.4x10 <sup>-3</sup> torr	: 9.7x10 <sup>-3</sup> torr
	%	%	%
CH <sub>4</sub>	70.7 ± 3.4	49.8 ± 2.7	54.0 ± 1.3
C <sub>2</sub> H <sub>6</sub>	13.0 ± 2.0	14.3 ± 2.7	13.1 ± 1.2
C <sub>3</sub> H <sub>8</sub>	7.4 ± 0.4	13.4 ± 1.1	11.7 ± 0.3
iso-C <sub>4</sub> H <sub>10</sub>	3.6 ± 1.9	7.5 ± 1.6	8.9 ± 1.2
n-C <sub>4</sub> H <sub>10</sub>	3.6 ± 0.9	6.0 ± 0.7	6.8 ± 0.8
Cis-2-butene	3.8*	4.2 ± 1.5	1.5 ± 0.5
Unidentified	---	5.8 ± 2.5	4.0 ± 0.3
Relative total yield	124 ± 36	252 ± 48	245 ± 22

\* Out of five reactions this compound was observed only in two reactions at 3.2x10<sup>-3</sup> torr pressure.

Table 4. Products of hydrogen atom reactions with graphite at 77°K. Effect of variation of reaction time. Hydrogen pressure 3.2x10<sup>-3</sup> torr and filament temperature 1590°C.

Product	Reaction Time		
	: 2 min	: 4 min	: 6 min
	%	%	%
CH <sub>4</sub>	73.5 ± 0.6	52.4 ± 2.0	61.8 ± 5.0
C <sub>2</sub> H <sub>6</sub>	11.2 ± 1.0	6.5 ± 3.3	10.0 ± 0.9
C <sub>3</sub> H <sub>8</sub>	9.3 ± 0.5	15.1 ± 3.9	10.9 ± 0.5
iso-C <sub>4</sub> H <sub>10</sub>	0.8 ± 0.6	5.9 ± 0.5	4.6 ± 0.2
n-C <sub>4</sub> H <sub>10</sub>	5.2 ± 1.5	18.3 ± 6.0	9.9 ± 3.9
Unidentified	---	1.8 ± 1.0	1.8 ± 0.1
Cis-2-butene	---	---	1.9*
Relative total yield	54.5 ± 14	219 ± 21	269 ± 28

\* Observed only in one of the four reactions.

Table 5. Products of hydrogen atom reactions with graphite at 77°K. Effect of thermalizing H-atoms to 300°K and 77°K. Initial hydrogen pressure  $6.4 \times 10^{-3}$  torr; reaction time 5 minutes; helium pressure about 0.13 torr.

Product	Thermal atoms*			Hot atoms**		
	77°K	300°K	%	77°K	300°K	%
CH <sub>4</sub>	89.4 ± 1.2	71.0 ± 0.2		60.4 ± 3.9		63.8 ± 0.1
C <sub>2</sub> H <sub>6</sub>	10.6 ± 1.1	12.8 ± 0.8		13.6 ± 0.7		10.2 ± 0.4
C <sub>3</sub> H <sub>8</sub>	-	7.9 ± 0.1		9.4 ± 1.3		12.0 ± 0.8
cis-2-butene	-	-		-		-
n-C <sub>4</sub> H <sub>10</sub>	-	4.1 ± 1.2		14.0 ± 5.4		8.2 ± 0.3
iso-C <sub>4</sub> H <sub>10</sub>	-	4.2 ± 1.2		2.6 ± 0.5		5.8 ± 0.6
Relative total yield	66 ± 2	70 ± 4		198 ± 58		211 ± 23

\* Helium present at a pressure of about 0.13 torr.

\*\*No helium present.

be retained by the carbon target even at 250°C and under vacuum. To find the amount of these solids an experiment was carried out as follows:

Graphite was powdered and stuck to a glass surface with water glass to form the target. A reaction was run at a filament temperature of 1560°C and a hydrogen pressure of  $3.2 \times 10^{-3}$  torr. After removing the gaseous products as described previously, the graphite was scraped off with a knife and washed with benzene. The washings were collected and counted in a liquid scintillation counter. It was found that the high molecular weight solids constituted about 50% of the total reaction products.

#### DISCUSSION

The reaction of hydrogen atoms with elemental carbon results in the formation of several saturated hydrocarbons: methane, ethane, propane, n-butane and isobutane. Along with these saturated hydrocarbons, occasionally cis-2-butene was detected. However, cis-2-butene was not formed in all reactions. Only the reactions at higher filament temperatures and higher hydrogen pressures gave cis-2-butene. At higher hydrogen pressures sometimes a peak appeared (2-6%) on the chromatogram which was not identified. In addition to the gaseous products some high molecular weight compound(s) (perhaps polymeric) were detected embedded in the carbon surface even at 250°C under vacuum. The amount of radioactivity present in these high molecular weight compounds was approximately 50% of the total reaction yield.



Thermodynamic functions,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  have been calculated for various reactions to determine if the reactions were thermodynamically favorable. To calculate  $\Delta H^\circ$  at 77°K the relation

$$\Delta H^\circ_{77} = \Delta H^\circ_{298.16} - \int_{77^\circ\text{K}}^{298.16^\circ\text{K}} \Delta C_p \cdot dt$$

was used. The integral was evaluated graphically. The molar entropy values were obtained using

$$\bar{S}^\circ = 2.303 \int_{\log T_1}^{\log 77^\circ\text{K}} \bar{C}_d \log T$$

where  $T_1$  is the Debye temperature. The integral was evaluated graphically. The value of entropy in the Debye region was taken from literature as mentioned in Table 6. The change in the Gibb's free energy was calculated using the relation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Due to unavailability to the author of heat capacity data for methane at low temperatures, the functions  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  could not be calculated at 77°K. At room temperature (298.16°K) the  $\Delta G^\circ$  for the reaction  $\text{C} + 4\text{H} \rightarrow \text{CH}_4$  is -206.4 kcal/mole. For ethane the  $\Delta G^\circ$  at 298.16°K is -299.8 kcal/mole. So it can be expected that  $\Delta G^\circ$  for methane will be more negative than -206.4 kcal/mole at 77°K.

As we can see from the values of  $\Delta G^\circ$ , the processes are thermodynamically favorable, even with atoms thermalized to 77°K.



Table 6. Thermodynamic functions ( $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$ ) for the formation of hydrocarbons from carbon and H-atoms at 77°K.

	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$	Source
	Kcal/ mole	cal.deg <sup>-1</sup> mole <sup>-1</sup>	Kcal/ mole	(s) of data
C + 4H → CH <sub>4</sub> <sup>*</sup> (s) (g) (g)	-226.2	-66.4	-206.4	
2C + 6H → C <sub>2</sub> H <sub>6</sub> (s) (g) (s)	-333.2	-122.8	-323.8	13, 14
3C + 8H → C <sub>3</sub> H <sub>8</sub> (s) (g) (s)	-442.0	-169.1	-429.0	15
4C + 10H → n-C <sub>4</sub> H <sub>10</sub> (s) (g) (s)	-551.9	-208.4	-535.8	16
4C + 10H → iso-C <sub>4</sub> H <sub>10</sub> (s) (g) (s)	-552.4	-207.8	-536.4	17

\* The values for methane are given at room temperature.

From the data presented in Tables 2-5, the following conclusions are proposed:

a. The initial product of hydrogen atom reactions with elemental carbon is methane (and possibly some ethane) which is then converted to a series of saturated hydrocarbons by a sequence of hydrogen atom and free radical reactions.

b. The processes by which methane and ethane are converted into higher molecular weight hydrocarbons have activation energies of several kcal/mole and can only occur with significant rates with hot H-atoms.

These conclusions can be supported by the following observed facts:

1. Effect of filament temperature: Both the rate of formation and energy distribution of hydrogen atoms are dependent upon the filament temperature. A Maxwell distribution of energies was indicated in a recent publication (18) on the angular distribution of H atoms emanating from a tungsten surface. The intensity varied directly with the cosine of the angle with the normal to the surface. This behavior was interpreted as a support to the belief that the H atoms were in thermal equilibrium with the tungsten surface when they left it. Table 2 shows that the percentage of methane in products decreases as the filament temperature is increased. In the case of graphite,  $\text{CH}_4$  was 81.0% at  $1400^\circ\text{C}$ , 63.5% at  $1670^\circ\text{C}$  and 55.1% at  $2037^\circ\text{C}$ . A similar trend was observed for diamond and carbon black. However, the total yield of the products (measured from areas under the chromatogram curves) increased with filament temperature as expected. For reactions with graphite, the relative reaction yield was 47, 130 and 212 at filament temperatures of  $1400^\circ$ ,  $1670^\circ$  and  $2037^\circ\text{C}$ , respectively.

2. Effect of hydrogen pressure: From Table 3 it is clear that the percentage of methane decreases when the hydrogen pressure is increased. This indicates that as the number of hydrogen atoms is increased a greater percentage of methane is converted into hydrocarbons of higher molecular weight. The relative total yield of the reaction products increased from 124 at  $3.2 \times 10^{-3}$  torr to 252 at  $6.4 \times 10^{-3}$  torr.

3. Effect of length of reaction time: A similar trend

(however not very regular) indicating the conversion of methane into higher molecular weight products is shown by the time studies (Table 4). With increasing reaction time the percentage of methane again decreases whereas the total relative yield of the products increases.

4. Effect of helium moderator: To determine if some of these reactions really require hot atoms, some experiments were run with thermalized hydrogen atoms. The data in Table 5 show that when the H-atoms were thermalized to  $77^{\circ}\text{K}$ , only methane and a small amount of ethane ( $\sim 10\%$ ) was formed. Thermal atoms at room temperature ( $300^{\circ}\text{K}$ ) gave some higher molecular weight hydrocarbons too, but the reaction yields from thermalized atoms were threefold smaller than those from hot atom reactions under similar conditions.

Other workers, from their studies of the hydrogen atom reactions with carbon, have suggested that gaseous carbon atoms take part in the formation of methane and subsequent products. These workers produced H-atoms with a microwave discharge, and the temperature of carbon was around  $900^{\circ}\text{C}$ . In the present work with the carbon target kept at  $77^{\circ}\text{K}$ , it is hard to imagine that there are any gaseous carbon atoms taking part in the reactions.

Assuming that the target temperature is  $77^{\circ}\text{K}$ , it is plausible to say that all the reactions occur at the surface because when methane is first formed it will be adsorbed on the target. With subsequent reactions it is converted to high molecular weight hydrocarbons at the surface of the target. Moreover, as

it has already been mentioned, hot atoms are required to convert methane to higher molecular weight hydrocarbons. If the hydrogen atoms penetrate the carbon before reacting, they would not have enough energy to abstract hydrogen from methane to form the intermediates in the subsequent formation of higher molecular weight hydrocarbons.



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HYDROGEN ATOM REACTIONS WITH  
ELEMENTAL CARBON AT 77°K

by

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AN ABSTRACT OF A THESIS

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This work was undertaken to study H-atom reactions with various forms of carbon (graphite, carbon black and diamond). The effect of variation of the energy of hydrogen atoms on products was studied. Also the reactions were carried out using varying pressures of hydrogen.

Hydrogen gas containing tritium was prepared by reducing tritiated water with zinc dust at  $650^{\circ}\text{C}$ . The hydrogen was atomized using a hot tungsten filament. The temperature of the filament was varied between 1673 and  $2310^{\circ}\text{K}$ . The pressure of hydrogen was varied in the range 3.2-9.7 microns. The usual reaction time was five minutes. The products were entrapped in a sampler cooled by liquid nitrogen. The sampler had two U-tubes in series; the one farther removed from the reaction vessel contained Linde type 5A Molecular Sieve for entrapping hydrogen and methane. The products were analyzed using a gas chromatograph and a proportional counter.

The main products of reaction of hydrogen atoms with all three forms of carbon used were  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $n\text{-C}_4\text{H}_{10}$  and  $\text{iso-C}_4\text{H}_{10}$ . The total yield of products increased with increasing filament temperature or pressure of hydrogen. The relative yield of methane was reduced with increasing filament temperature and also with increasing hydrogen pressure. Time studies showed that the percentage of methane fell with an increase in reaction time whereas the total yield of the products increased. All these observations can be explained as follows. The initial product of hydrogen atom reactions with elemental carbon is



methane (and possibly some ethane) which is then converted to a series of saturated hydrocarbons by a sequence of hydrogen atom and free radical reactions. The reactions with hydrogen atoms thermalized to 77°K gave only methane in relatively low yield and ethane ( 10% of methane yield). Evidently the processes by which these two compounds are converted into higher molecular weight hydrocarbons have activation energies of several kcal and can only occur with hot atoms.